

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No. : 10/829,598 Confirmation No.: 6855
Applicant : Graetz et al.
Filed : April 22, 2004
TC/A.U. : 1795
Examiner : Hodge, Robert W.
For : High-Capacity Nanostructured Germanium-Containing Materials
and Lithium Alloys Thereof
Docket No. : 27-06
Customer No.: 23713

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION OF JASON GRAETZ UNDER 37 CFR 1.132

Sir:

Jason Graetz hereby declares as follows:

1. I, Jason Graetz, am an inventor of the above-identified patent application.
2. I am presently a materials scientist with Brookhaven National Laboratory.
3. I have experience and expertise in the field of materials science and synthesis of thin film and nanoscale materials.
4. This declaration provides evidence to establish that electrodes of nanofilms of silicon-germanium framework material deposited on a metal substrate displayed greater capacity stability with increasing cycling rates over the cycling rate range from 0.04 to 1 C or 0.04 C to 5 C compared to electrodes including nanofilms of silicon framework material deposited on a metal substrate. As defined at para. [0040] of the specification as filed, the term framework material refers to a material into which an electrochemically active species can reversibly enter and exit.
5. As described in Example 9 (page 25) of the present application, silicon-germanium nanofilms were deposited on metal substrates by evaporation and physical deposition of elemental silicon and elemental germanium. The stoichiometries of the silicon and germanium starting materials were

$\text{Si}_{0.25}\text{Ge}_{0.75}$, $\text{Si}_{0.5}\text{Ge}_{0.5}$ and $\text{Si}_{0.75}\text{Ge}_{0.25}$. The stoichiometries of the resulting films are assumed to be the same as those of the starting materials. Silicon nanofilms and germanium nanofilms were also deposited on metal substrates by evaporation and physical deposition.

6. Test cells were constructed with the nanofilm on the substrate as one electrode of a 2016 coin cell and lithium metal as a counter electrode. An equimolar mixture of ethylene carbonate and dimethyl carbonate with LiPF₆ was used as the electrolyte. A separator was placed between the two electrodes. Electrochemical tests were performed using an Arbin Instruments BT2000 battery cycler. During discharging of this test cell, lithium ions are released from the lithium electrode and lithium is incorporated into the nanostructured film, electrochemically forming a lithium alloy. During charging of the test cell, lithium ions are released from this lithium alloy. Therefore, the nanofilm material acts as a framework material into which lithium species can reversibly enter and exit. The data from these electrochemical tests suggests that the silicon-germanium, silicon and germanium films were all amorphous.
7. Figure 12 of the application, attached as Figure A of this declaration, shows the capacity versus cycling rate for nanofilms of silicon-germanium framework material, as well as for nanofilms of silicon framework material and nanofilms of germanium framework material. The material was cycled five times before the test at the lowest cycling rate shown. In general, the capacities were similar for the charge and discharge steps; the capacities shown in the plot are believed to be for the charge step (delithiation of the lithium alloy of the framework material). Figure A shows that over the range 0.04 C to 1 C, the loss in capacity for the silicon framework material was approximately 7% of the 0.04 C value, while the loss in capacity for the 25% Ge framework material, the 50% Ge framework material and the 75% Ge framework material was approximately 3%, 6%, and 2%, respectively (as determined from the curves fitted to the data points). Figure A shows that over the range 0.04 C to 5 C, the loss in capacity for the silicon framework material was approximately 31% of the 0.04 C value, while the loss in capacity for the 50% Ge framework material and the 75% Ge framework material was approximately 15% and 19%, respectively (as determined from the curves fitted to the data points). Figure A also shows that up to a cycling rate of about 4 C, the capacity of the 25%, 50% and 75% Ge alloy framework materials are higher than that of the Ge framework material for a given cycling rate.
8. Attached Figure B of the declaration shows the charge/discharge capacities for 60 nm films of 100% silicon and 75 mole% silicon and 25 mole% germanium cycled at a rate of 5C. Each electrode was pre-cycled four times at a moderate rate (C/4) before the high rate testing. The addition of germanium significantly reduced the loss in capacity with

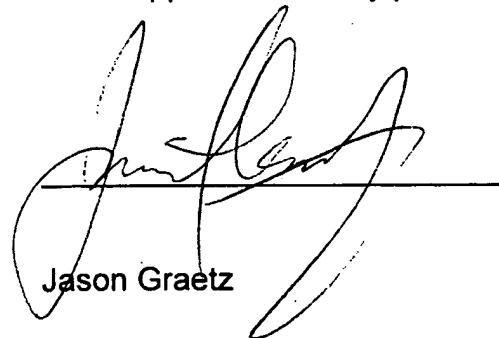
increasing number of cycles. In particular, the charge capacity loss was approximately 2% for the 25% Ge alloy and approximately 59% for Si at 10 cycles. The charge capacity loss was approximately 29% for the 25% Ge alloy and approximately 71% for Si at 65 cycles. The charge capacity of the 25% Ge electrode is greater than that of the Si electrode on the first charge cycle and for subsequent cycles shown in the plot.

9. In summary, electrodes with a nanofilm of silicon-germanium framework material in the composition range $\text{Si}_{(1-z)}\text{Ge}_z$, wherein z is from 0.25 to 0.75 displayed improved performance compared to electrodes with a nanofilm of silicon framework material. Nanofilms of silicon-germanium framework material displayed reduced capacity loss with increasing cycling rates compared to nanofilms of silicon framework material over the cycling rate range from 0.04 to 1 C or 0.04 C to 5 C. Lithium alloys of the silicon-germanium nanofilms also displayed reduced capacity loss with increasing cycling rates compared to lithium alloys of the nanofilms of silicon framework material over the cycling rate range from 0.04 to 1 C or 0.04 C to 5 C. Reduced capacity loss is equivalent to improved capacity stability. In addition, nanofilms of a 25% Ge alloy framework material showed reduced capacity loss with increasing cycle number at a cycle rate of 5C at both 10 and 65 cycles as compared to nanofilms of silicon framework material.
10. This declaration also provides evidence that the increased capacity stability with increasing cycling rate of electrodes including nanofilms of silicon-germanium framework material compared to electrodes including nanofilms of silicon framework material is unexpected in view of the disclosure provided by WO 01/96847 (Zhou et al.). The Zhou reference is of record in the present application.
11. The Zhou reference discloses nanostructures formed from silicon and nanostructures formed from germanium (page 4, about lines 20-21). This reference also discloses an electrochemical cell with a lithium foil electrode and nanostructure film deposited on a stainless steel substrate as the second electrode (page 7, about lines 3-5). Although p. 8 (about lines 8-10) of the reference states that "the nanostructure-lithium material of the present invention exhibits high capacities, even when charged/discharged at high rates," the reference does not teach or suggest that the capacity stability with increasing cycling rates of germanium nanostructure-based materials is superior to that of silicon nanostructure-based materials. The reference also does not teach or suggest that combination of germanium nanostructures with silicon nanostructures would produce an improvement in capacity stability with increasing cycling rates. Therefore, the improved capacity stability with increasing cycling rate over the cycling rate range 0.04 to 1 C or 0.04 C to 5 C of the silicon-germanium nanofilm of amended claim 64 and the alkali

metal alloy of the silicon-germanium nanofilm of amended claim 66 is unexpected in view of the disclosure of Zhou.

12. This declaration also provides evidence that the increased capacity stability with increasing cycling rate at cycling rates of electrodes including nanostructured films of silicon-germanium framework material compared to electrodes including nanostructured films of silicon framework material is unexpected in view of the disclosure provided by US 2003/0054242 A1 (Kusumoto et al.). The Kusumoto reference is of record in the present application.
13. The Kusumoto reference discloses negative electrodes containing a Li-Si alloy or a Li-Ge alloy (para. [0015]). Para. [0050] of the reference describes Si film thicknesses of 2 to 10 microns. The reference does not teach or suggest that the capacity stability with increasing cycling rates of germanium films or nanofilms is superior to that of silicon films or nanofilms. The reference also does not teach or suggest that combination of germanium with silicon would produce an improvement in capacity stability with increasing cycling rates. Therefore, the improved capacity stability with increasing cycling rate over the cycling rate range 0.04 to 1 C or 0.04 C to 5 C of the silicon-germanium nanofilm of amended claim 64 and the alkali metal alloy of the silicon-germanium nanofilm of amended claim 66 is unexpected in view of the disclosure of Kusumoto.
14. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above-referenced application or any patent issuing thereon.

Date: 02/16/10



A handwritten signature in black ink, appearing to read "Jason Graetz", is written over a horizontal line. The signature is fluid and cursive, with a large, stylized 'J' at the beginning.

Jason Graetz

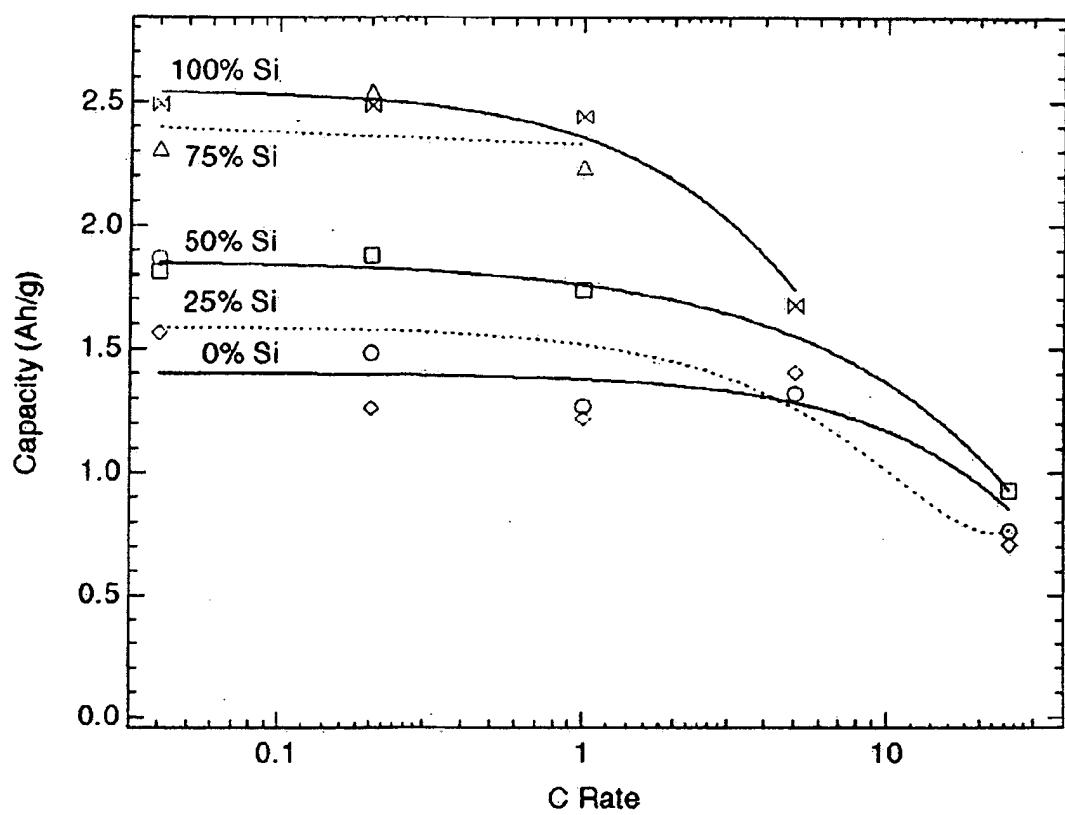


Figure A

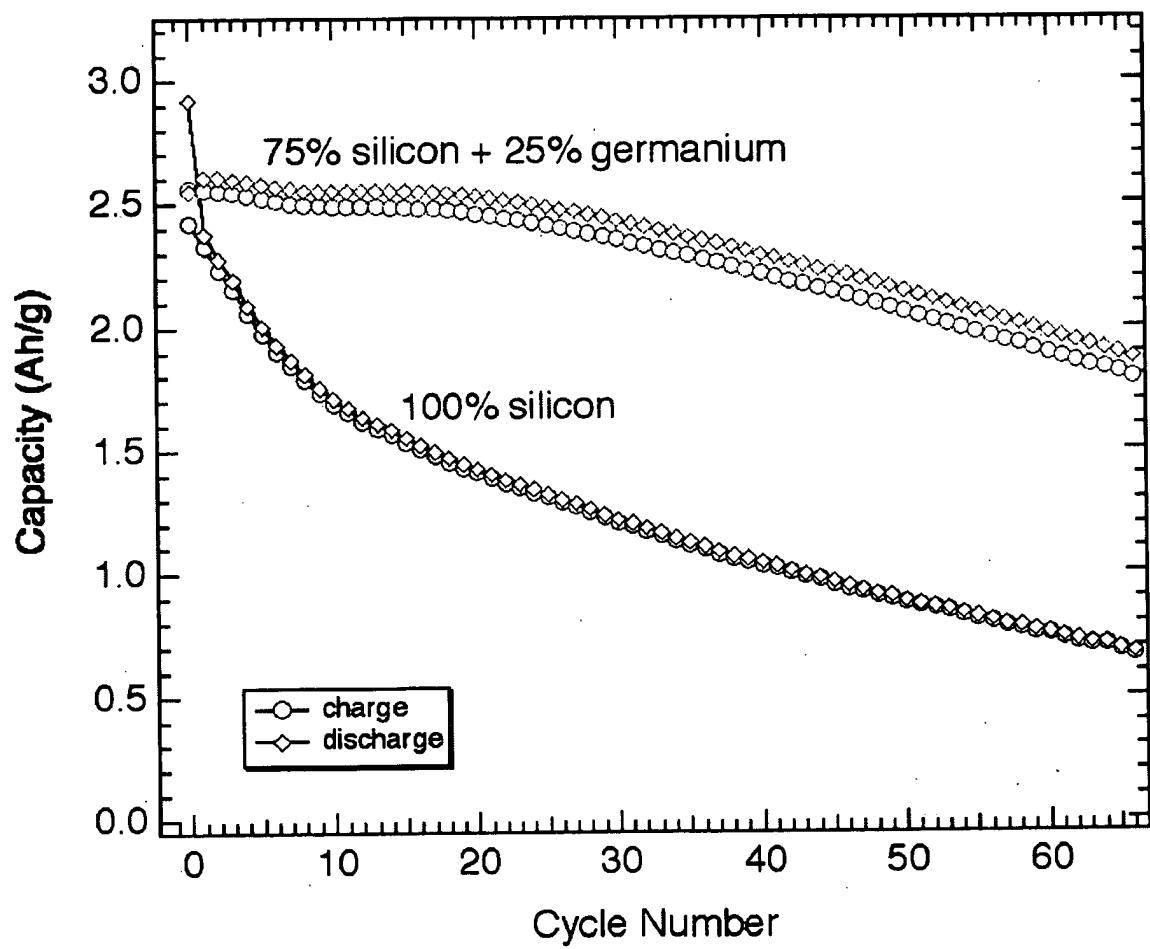


Figure B